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## STRUCTURAL TRANSFORMATIONS DURING HEAT-TREATMENT OF QUARTZ CERAMIC

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The microhardness of quartz ceramic was measured at three stages of heat-treatment of the primary green part obtained by slip casting — after drying at 100°C, after sintering at 1190°C and after flame treatment of the surface. Although the final hardness is close to the known values for quartz glass, IR spectroscopy indicates the presence of significant internal stresses in the material. The high content of the end atomic groupings found in the primary material is a favorable factor for doping kersil.

**Key words:** quartz ceramic, heat-treatment, microhardness, IR spectra.

Quartz ceramic produced under the trade name 'kersil' [1] finds applications in many areas of industry ranging from the production of decorative materials [2] and different refractory articles to reflectors for lamps used to pump solid-state lasers [3]. Kersil is obtained from finely disperse quartz glass by means of water slip casting in a gypsum mold. The primary green part passes through a series of successive heat-treatment cycles after preliminary soaking at room temperature for slow drying. The finished part is formed during subsequent drying at 100–150°C, calcining at 1150–1200°C and flame treatment of the surface by an oxygen-hydrogen burner.

Even though the technology used to fabricate this ceramic is well known [1] there is little published information on the physical-mechanical properties of the material at different stages of heat-treatment, and as far as we know there are no data on the evolution of the structure of the silicon-oxygen framework of the glass. In the present work some characteristics of the green parts and the finished ceramic part, knowledge of which could be helpful for controlling the properties of the final product at intermediate stages of its production, were determined. To this end measurements of the microhardness were performed and the IR reflection spectra of the material were recorded after each temperature cycle. Similar parameters of a monolithic quartz glass are presented for comparison. Disks with diameter 60 mm and thickness 10 mm served as samples.

The reflection spectra were recorded with an IR Prestige-21 IR-Fourier spectrometer (angle of incidence 10°).

The microhardness was determined by making indentations with a Vickers diamond pyramid with vertex angle 136°. The measurements were performed with load 0.98 N on the indenter.

The hardness of porous ceramic is determined mainly by interparticle bridges [4], on whose number and strength the resistance of the material to the penetration of the indenter depends. The IR-spectra make it possible to evaluate the connectedness of the silicate network and determine the presence of internal stresses in the samples.

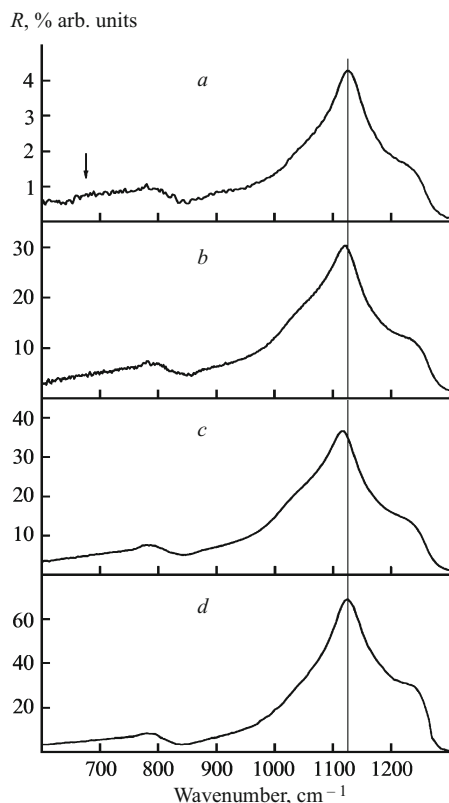
The microhardness of the starting material turned out to be very low, varying in magnitude in different sections of the sample from 0.28 to 0.37 GPa. We note that because in measurements of the microhardness the indentations comprise tens of microns this method reveals the structural nonuniformity in different sections of the material. The low values of the microhardness indicate weak bridges between SiO<sub>2</sub> particles, which in incompletely calcined material are bound only by cohesion forces.

The microhardness of the material calcined at 1190°C turned out to be an order of magnitude higher than that of the initial material. The microhardness varied from 4.6 to 5.7 GPa on different sections of the sample. Even in this sample the variance in the microhardness attests to structural nonuniformity. Local fracture of the material was observed in the indentation zone, indicating the presence of residual stresses in the sample. In individual cases it was impossible to measure the diagonal of the imprint because of strong fracture occurring as the indenter was extracted.

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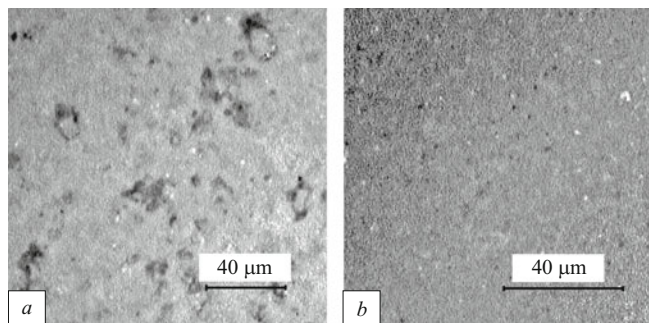
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**Fig. 1.** Reflection spectra  $R$  of quartz ceramic in the region  $600 - 1300 \text{ cm}^{-1}$  after drying of the green part at temperature  $100^\circ\text{C}$  (*a*), calcining at  $1190^\circ\text{C}$  (*b*) and subsequent flame treatment of the surface of the sample (*c*); *d*) spectrum of monolithic quartz glass. The vertical line shows the position of the  $1122 \text{ cm}^{-1}$  band in quartz glass.

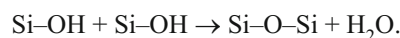
The microhardness of the sample whose surface was 'vitrified' by flame treatment was found to be  $7.6 \pm 2.5 \text{ GPa}$ , which is close to the published data on the hardness of quartz glass [5]. However, fracture is also observed in the imprint zone, showing that the glassy material is in a stressed state.

IR-Spectroscopy confirms the presence of internal stresses. The Fourier reflection spectra are presented in Fig. 1. The strongest band in the spectrum of the intermediate product dried at  $100^\circ\text{C}$ , which belongs to the vibrations of the oxygen atom in Si–O–Si bridge groups [6], lies at  $1122 \text{ cm}^{-1}$  (Fig. 1*a*), just as in the spectrum of monolithic quartz glass (Fig. 1*d*). After each stage of heat treatment of the samples, a low-frequency shift of this band is observed in their spectra. After a sample is calcined the band shifts to  $1118 \text{ cm}^{-1}$  (Fig. 1*b*), and after flame treatment its frequency decreases to  $1115 \text{ cm}^{-1}$  (Fig. 1*c*). A decrease in the vibrational frequency of the oxygen atom in the Si–O–Si bridges was previously observed by applying tensile stress to quartz glass plates [7]. On this basis it can be assumed that calcination and flame treatment increase the internal stress in a ceramic. Ordinarily, as a result of high-temperature annealing the internal stresses relax and the solid is in a more equilib-



**Fig. 2.** Photographs of kersil before (*a*) and after (*b*) calcination at temperature  $1190^\circ\text{C}$ ;  $\times 200$ .

rium state. However, in the case of porous silica saturated with bound water heat-treatment is accompanied by intense de-watering of the interior of the sample. The water is formed in the reaction



The connectedness of the material increases, but significant tensile stresses appear at the same time.

The presence of Si–OH end groups in the structure of the primary material is confirmed by a wide band in the region  $600 - 800 \text{ cm}^{-1}$ . According to [6] this band belongs to groups of silicon atoms with non-bridge oxygen atoms, for example, of the type HO–Si–OH. In Fig. 1 it is evident that this band in the spectrum of the slowly dried material (Fig. 1*a*) is comparable in intensity to the band at  $790 \text{ cm}^{-1}$  belonging to the bridge structural groups; its intensity is appreciably lower after calcination at  $1190^\circ\text{C}$  (Fig. 1*b*), and in the vitrified layer it is almost invisible against the background due to the  $790 \text{ cm}^{-1}$  band (Fig. 1*c*), demonstrating structure close to quartz glass (Fig. 1*d*). The presence of a large number of non-bridge oxygen atoms in the intermediate product kersil, which was not heat-treated at high temperature, is associated with the fact that the  $\text{SiO}_2$  particles in the water suspension enter into hydrolytic reactions with the formation of SiOH end groupings, and the material partially gels. Residues of the gel inclusions are clearly seen in photographs of the sample after drying at  $100^\circ\text{C}$  (Fig. 2*a*). These inclusions vanish after calcination (Fig. 2*b*), but the nonuniformity of the material is noticeable in the photograph. Apparently, in both cases these structural nonuniformities are responsible for the large variance of the microhardness measurements.

In summary, IR-spectroscopy data indicate that internal stresses are present in the ceramic kersil. These stresses are a result of rapid release of residual water during heat-treatment at high-temperature. At the same time the presence of end atomic groupings in the primary material is a favorable factor for doping kersil, which is necessary for use in lamps to pump lasers.

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